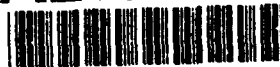


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Laser-Induced Dissociation of HN_3 (DN_3) on
GaAs (100) at 100 K

by

Y. Bu, L. Ma, and M. C. Lin

Department of Chemistry

Emory University

Atlanta, GA 30322

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Abstract

HN₃ (DN₃) molecularly adsorbed on GaAs (100) at 100 K and formed dimers at higher dosages (>20 L). Exposing the sample to 308 nm excimer laser radiation caused the dissociation of HN₃ into HN and N₂ species. The N₂, residual HN₃ and some HN species desorbed from the surface, as the irradiated sample was further annealed at 200 to 550 K. Both HREELS and XPS results indicated that NH species bonded to the As rather than the Ga atom on GaAs (100) under the present experimental conditions.

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Interaction of N-containing compounds, particularly NH_3 , with Si substrates have been studied extensively with different techniques^[1-10]; e.g. HREELS, UPS, XPS, STM and TPD, etc. Recently, several studies on the Si nitridation using N_2H_4 ^[11] and HN_3 ^[12-16] molecules have also been reported. On the other hand, fewer results appeared in the literature for such reactions with GaAs surfaces, probably due to the lower reactivity of the latter substrates. However, with the help of laser radiation, NH_3 was found to dissociate into NH_x and H species on the GaAs (100) surface.^[17] Here we report the preliminary results of laser-induced dissociation of HN_3 on GaAs (100) at 100 K, studied with HREELS, UPS and XPS.

The experiments were carried out in a custom-designed UHV system equipped with multiple surface analysis capabilities, as described elsewhere^[11,12]. The GaAs substrate from Laser Diode Inc. was cut into $1.5 \times 1.0 \text{ cm}^2$ samples. These samples were then cleaned with a 300 eV Ar^+ beam for 30 minutes followed by annealing at 770 K for a few minutes. HN_3 (DN_3) samples were prepared in the same manner as reported previously.^[12,14]

When 20-L HN_3 was dosed onto GaAs (100) at 100 K, HREELS produced peaks at 56, 152, 270 and 394 meV, as shown in Figure 1. By analogy to the IR results of HN_3 in the gas phase^[18] or in solid N_2 ^[19] and the HREELS results of HN_3 on Si

substrates,[12,14] these peaks could be assigned to the individual HN_3 molecular vibrations as listed in Table 1. The strong peak at 36 meV is due to the surface optical phonon loss. After exposing the sample to 308 nm excimer laser radiation operated at 20 mJ/cm² · pulse and 10 Hz for 60 minutes, all molecular vibrational features disappeared. Instead, peaks at 128, 160, 196, 265 and 420 meV were present. The 160 and 420 meV modes could be assigned to the deformation and stretching vibrations of the NH species, while that of the 196 meV peak to the stretching vibration of the N_2 species with a bond order of 2.[16] These changes obviously indicated the dissociation of the HN_3 into NH and N_2 species. On the other hand, the 128 meV peak could be attributed to the AsN stretching mode. Such a peak was also observed in IR for dissociatively adsorbed NO_2 [20] and in HREELS for NO[21] on GaAs surfaces. The remaining peak at 265 meV may have contributions from both As-H and $\text{N}\equiv\text{N}$ stretching vibration, as will be discussed later. It should be pointed out that the low energy loss peaks are due to the single and double phonon losses.

Further examination of the laser effect was also carried out with DN_3 HREELS and HN_3 UPS. As shown in Figure 2, when 20 L DN_3 was dosed on the surface, peaks at 52, 117, 150, 270, 300, 387 and 413 meV (shoulder) were observed in HREELS. This spectrum was rather complicated because of the coexistence of both

DN₃ and HN₃ with possible dimer formation on the surface. Nevertheless, these peaks could be sorted out by comparing with the corresponding HN₃ results, as listed in Table 1. When this sample was exposed to 308 nm laser radiation at 10 mJ/cm² pulse and 10 Hz for 30 minutes, the observed changes indicated a partial desorption of the adsorbates and, as expected, the decomposition of DN₃ (HN₃). The partial desorption is reflected by the obvious attenuation of all peak intensities, while the dissociation of the DN₃ (HN₃) is evidenced by the appearance of the 200 meV peak, the shift of the 150 and 270 meV peaks to 155 and 255 meV, the decrease of the 387 meV and the increase of the 413 meV peak intensities. The 200 meV peak is due to the adsorbed N₂ species, and this observation is consistent with the relative intensity increase of the 413 meV peak, which is now shifted to 418 meV due to the formation of the NH species. On the other hand, the peak shift of the 150 and 270 meV modes suggests that the remaining adsorbed DN₃ (HN₃) molecules bonded more strongly to the surface atoms. The 155 meV peak may also have some contributions from the NH deformation mode. This became more obvious as the sample was further irradiated with the laser for an additional 30 minutes. The additional irradiation shifted the 155 meV peak further to 162 meV due mainly to the deformation vibration of the NH species, while that of the DN species was observed at 126 meV, which should also

have some contributions from the AsN stretching mode, as discussed in the HN₃ results. The corresponding ND (NH) stretching mode appeared at 308 (418) meV. In addition, the 255 meV peak shrank considerably due to the more extensive dissociation and desorption of the DN₃ (HN₃) molecules. Since there are no intense peaks at 230 and 260 meV, expected for GaH and AsH stretching vibrations,^[15] respectively, it is concluded that no appreciable breaking of the HN (DN) bond occurred under these experimental conditions. This would also rule out the possibility that the 200 meV peak is due mainly to the As-D species, as the relative intensity of 262 meV peak was weak and the stretching mode of NH is more intense than that of ND. Furthermore, the intensity ratio of the 250 meV to the 420 meV mode is smaller in the HN₃ (Figure 1) than that in the corresponding DN₃ (HN₃) HREEL spectra (Figure 2), because of the use of a less intense laser radiation in the latter experiment. This peak intensity ratio difference, in turn, suggests that the partial NH bond cracking occurred in the HN₃ experiments and so the 265 meV peak in Figure 1 has contributions from the As-H stretching vibration.

Finally, the slight attenuation of the 200 meV peak is due to the partial desorption of the N₂ species. A simultaneous measurement of gas-phase products could certainly provide more information about the laser irradiation process.

Unfortunately, such a measurement could not be performed in the present experimental setup.

Figure 3 illustrates the effect of laser irradiation on the a 20 L HN_3 dosed GaAs (100) by He(II) UPS analysis. After dosing HN_3 at 100 K, peaks at 4.4, 6.2, 9.5, 10.5 and 14.0 eV below E_F were noted. In a He(I) UP spectrum of the gaseous HN_3 ,^[22] peaks at 10.7, 12.2, 15.5 and 16.8 eV below E_V were observed and assigned to the out-of-plane, the in-plane non-bonding π orbital, the $p\sigma$ and the bonding π orbitals, respectively. These results agree well with those of HN_3 on GaAs (100) observed here, if a value of 6.3 eV for the surface work function and the relaxation of the molecules upon the adsorption is taken into account. The peak due to the NH bonding orbital was not shown in the gaseous HN_3 UP spectrum; however, it was clearly shown in the spectrum taken from HN_3 condensed on an Au surface at an energy of 20.1 eV below E_V .^[23] This value is also consistent with the 14.0 eV peak below E_F for HN_3 adsorbed on GaAs. Finally, a noticeable but small peak at 3.0 eV is probably due to the H-bonded N lone electron pairs. The formation of an H-bond could cause a charge redistribution in the HN_3 molecule, which tends to lower the binding energy of the N lone electron pair.^[24] Since these electron pairs are shared by the H atom of

the adjacent HN_3 molecule, the corresponding photoelectron signal intensity should be weak as expected.

When this 20 L HN_3 dosed GaAs was irradiated by the 308 nm excimer laser (10 mJ/cm^2 pulse and 10 Hz) for 30 minutes, two broad peaks centered at 7 and 10 eV with a hump at 8 eV were present in the UP spectrum due to the convolution of the different orbitals in the various adsorbed species, as discussed in the DN_3 (HN_3) HREELS results. When this sample was annealed at 200 and 550 K, three peaks at 4.5, 6.5 and 9.9 eV and a hump at 13.7 eV were noted. These features could probably be attributed to the NH_x ($x = 0,1$) species left on the surface by analogy to the corresponding UPS results of NH_x species on Si substrates.[11] In the latter case three peaks at 4, 7, and 10 eV below E_F were observed.

Similar experiments were also performed by using the XPS technique; the results are shown in Figure 4a and 4b for N_{1s} and $\text{As } 2\text{P}_{2/3}$ photoelectrons, respectively. As 20 L HN_3 was dosed on GaAs at 100 K, the N_{1s} XPS produced two peaks at 404.2 and 400.2 eV, which could be attributed to the N^{II} and N^{I} plus N^{III} photoelectrons, respectively. Here the nitrogen atoms in HN_3 are labeled according to $\text{HN}^{\text{I}} \text{N}^{\text{II}} \text{N}^{\text{III}}$. The larger and broader 400.2 eV peak can actually be deconvoluted into two peaks, because of the different chemical environments of the N^{I} and N^{III} atoms.

This has been discussed in detail in the N_{1s} XPS for both HN_3 condensed on Au^[23] and adsorbed on Si surfaces.^[14] Exposing this sample to 308 nm excimer laser radiation (10 mJ/cm² pulse and 10 Hz) for 60 minutes shifted the two peaks to 402.7 and 398.7 eV, respectively. The 398.7 eV peak could be attributed to the NH species, while the 402.7 peak to the adsorbed N_2 and probably some residual HN_3 molecules. Annealing this sample to 200-550 K eliminated the 402.7 eV peak and attenuated the 398.7 eV peak, because of the total and partial desorption of N_2 and NH, respectively.

While there was no change of the Ga $2P_{2/3}$ XPS peak in both the peak position and its full width at half maximum, an additional peak at 1325.6 eV was produced in As $2P_{2/3}$ XPS after one hour laser irradiation of the 20 L HN_3 dosed GaAs. This peak, too high in binding energy to be attributed to the AsH species,^[25] indicated probably the formation of the AsN bond, which is also identified in the corresponding HREELS (the 128 meV peak) under similar experimental conditions. Annealing the sample from 220 to 550 K shifted the 1325.6 eV peak slightly to 1325.1 eV, which is also too high in binding energy for the excessive As on GaAs (100).^[25] This peak may be attributed to the presence of a small amount of As on the surface replaced by N atoms, as reported in a study of the atomic N reaction with GaAs (110)^[26]. It should be pointed out that when GaAs was treated with ammonium sulfide, the AsS rather than

the GaS species was formed, as evidenced also by the appearance of an additional high energy peak in the As $2P_{2/3}$ XP spectrum.[27]

In summary, HN_3 (DN_3) molecularly adsorbed on GaAs (100) at 100 K could be photo-dissociated into HN and N_2 species as the sample was exposed to a 308 excimer laser radiation for 60 minutes. Further annealing the sample to 200 and 550 K caused the desorption of the N_2 molecule, the residual HN_3 and some NH species. Both HREELS and XPS results indicate that NH_x ($x=0,1$) species bond to the As rather than the Ga atom on GaAs.

Acknowledgement

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Table I. Vibrational frequencies (in meV) and assignments of HN_3 and DN_3 in the gas phase and on GaAs (100)

Vibrational Mode	Gas phase (a)		On GaAs (100)(b)	
	HN_3	DN_3	HN_3	DN_3 (HN_3)
δ_a (NNN)	66	61	56(c)	52 (c,d)
δ_s (NNN)	75	73	-	-
ν_a (NNN)	143	147	152	150(d)
δ_a (HN)	157	118	152	117
ν_a (NNN)	265	262	270	270(d)
ν_s (NH)	414	307	394 ^c	300 (387/400)(c)

(a) Ref. 18, 19

(b) This work

(c) The peak has contribution from the dimeric HN_3 .

(d) The peak has contribution from the HN_3 .

Figure Captions

Figure 1. The effect of 308 nm excimer laser on HREELS of a 20 L HN_3 dosed GaAs (100) at 100 K; (a) before and (b) after laser irradiation at 20 mJ/cm^2 pulse and 10 Hz for 60 min.

Figure 2. HREELS of 20 L DN_3 dosed GaAs (100) at 100 K after exposure to 308 nm excimer laser for (a) 0, (b) 30, and (c) 60 min. operated at 10 mJ/cm^2 pulse and 10 Hz.

Figure 3. He(II) UPS of 20 L HN_3 on GaAs (100): (a) dosing at 100 K, (b) with 308 nm excimer laser irradiation (10 mJ/cm^2 pulse and 10 Hz for 30 minutes), (c) annealed at 220 K and (d) at 550 K after laser irradiation.

Figure 4. Laser irradiation and annealing effect on (a) N_{1s} and (b) $\text{As } 2\text{P}_{2/3}$ XPS taken from a 20 L HN_3 dosed GaAs (100).

